

Solid-phase extraction using hierarchical organosilicates for enhanced detection of nitroenergetic targets[†]

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A novel porous organosilicate material was evaluated for application as a solid phase extraction sorbent for preconcentration of nitroenergetic targets from aqueous solution prior to HPLC analysis. The performance of the sorbent in spiked deionized water, groundwater, and surface water was evaluated. Targets considered included 2,4,6-trinitrotoluene, 2,4-dinitrotoluene, RDX, HMX, and nitroglycerin. The sorbent was shown to provide improved performance over Sep-Pak RDX. The impact of complex matrices on target preconcentration by the sorbent was also found to be less dramatic than that observed for LiChrolut EN. The impact of changes in pH on target preconcentration was considered. Aqueous soil extracts generated from samples collected at sites of ordnance testing were also used to evaluate the materials. The results presented here demonstrate the potential of this novel sorbent for application as a solid phase extraction material for the preconcentration of nitroenergetic targets from aqueous solutions.

Introduction

Nitroenergetic compounds, including 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), RDX, HMX, and nitroglycerin (NG), are common components of ordnance with DNT and NG often found as propellants. Environmental contamination

by nitroenergetic compounds can result from a number of activities. On munitions testing, training, and disposal sites in the United States, the most common cause of residual contamination is device malfunction in which the nitroenergetic compounds are not fully utilized. These types of sites can be found at Massachusetts Military Reservation (MA, USA) and Holloman Air Force Base (NM, USA), for example. Contamination can also result from spillage of the compounds during ordnance manufacture, as is the case at Joliet Army Ammunition Plant (IL, USA). Contamination has also been noted to result from degradation of munitions left in the environment, for example, those disposed of by burying or dumping into bodies of water and unrecovered land mines. In these cases, there is contamination resulting from leakage of compounds as corrosion of the munitions housings progresses.¹

Offsite analysis of samples by a US Environmental Protection Agency (EPA) certified method continues to be the standard for evaluating these sites of potential contamination and for monitoring levels at sites of known contamination. The methods employ

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[†] Electronic supplementary information (ESI) available: Complete results of HPLC analysis for extraction of TNT, DNT, NG, RDX, and HMX from deionized water, artificial sea water, ground water, surface water, samples of varied pH, and soil sample extracts are provided in the ESI. Materials characterization data for the MMI organosilicate material, Sep-Pak, and LiChrolut EN are also provided. See DOI: 10.1039/c1em10034c.

Environmental impact

Environmental contamination by nitroenergetic compounds is of serious concern to populations surrounding the affected areas. Tracking the movement of these compounds through natural water sources is critical to formulation of appropriate restoration efforts and monitoring the success of such programs. The limited sensitivity of portable detection techniques necessitates the use of offsite analysis methods that are both costly and time consuming. Solid-phase extraction for preconcentration of targets provides the potential to resolve these sensitivity issues and offers methods for long-term remote monitoring as well as onsite real-time reporting on contaminant concentrations. The novel materials described here offer improved performance over commercially available sorbents and are reusable over hundreds of cycles.

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liquid or gas chromatography and do not lend themselves well to transition into portable devices and methods. This type of sample collection and analysis process is both expensive and time consuming. Onsite methods for monitoring contamination levels or as indicators of the need for further testing are desirable. Unfortunately, many portable methods either lack the robustness, ease of use, quantitative capability, or sensitivity necessary for field application.^{2–10} Methods developed for field applications typically rely on preconcentration of targets prior to analysis. As an example, the procedure outlined by the US EPA for colorimetric detection of TNT and RDX relies on adsorption of target from two litres of sample solution onto membranes functionalized with poly(styrene divinylbenzene) and octadecyl particles.^{11,12}

A number of reports have utilized different materials for solid phase extraction of nitroenergetic targets. The development of fiber-based solid-phase microextraction (SPME) protocols has been the subject of several efforts.^{13–21} These SPME methods are typically compatible with gas or liquid chromatography, and equilibration times can be lengthy. Other solid-phase extraction protocols have utilized a range of polymer materials and even clays in various formats providing preconcentration for ion mobility spectroscopy (IMS),^{22–24} spectrophotometric,^{11,25–27} and electrochemical²⁸ detection methods in addition to gas and liquid chromatography.^{29–36} Porous organosilicate materials offer a class of sorbents with the potential to provide the preconcentration necessary for utilization of portable detection techniques. These materials are organic/inorganic hybrids synthesized through condensation of organic group bearing siloxane precursors around surfactant micelles.^{37–40} The materials offer high surface areas and large pore volumes with the rugged character of silicates and the binding characteristics more typical of organic polymers.

Our previous efforts have focused on the synthesis of organosilicate materials and characterization of their interaction with nitroenergetic compounds.^{41,42} The materials were synthesized through co-condensation of bis(trimethoxysilyl)benzene (DEB) and 1,2-bis(trimethoxysilyl)ethane (BTE) (Fig. 1). Early materials were mesoporous and utilized Brij®76 micelles as the surfactant template.⁴¹ An imprinting technique in which the surfactant head groups were modified with a target analog was developed to provide enhanced binding capacity and selectivity in the materials. Subsequent efforts focused on altering the macroscale structure of the materials in order to reduce the resistance of the sorbents to flow of aqueous solutions and enhance diffusion throughout the available pore system.^{42,43} This new class of materials utilized Pluronic P123 (Fig. 1), a larger surfactant, and a swelling agent (mesitylene) to produce a hierarchical structure with both macro- and mesoscale morphology. These materials were shown to provide preconcentration of targets from laboratory samples prepared in deionized water. Here, we demonstrate the applicability of the sorbents to preconcentration of nitroenergetic targets in real-world matrices and compare their performance to that of two commercially available sorbents, LiChrolut EN and Sep-Pak RDX.

Results and discussion

Five targets, TNT, RDX, HMX, DNT, and NG (Fig. 1), were selected based on their relevance to water quality in regions

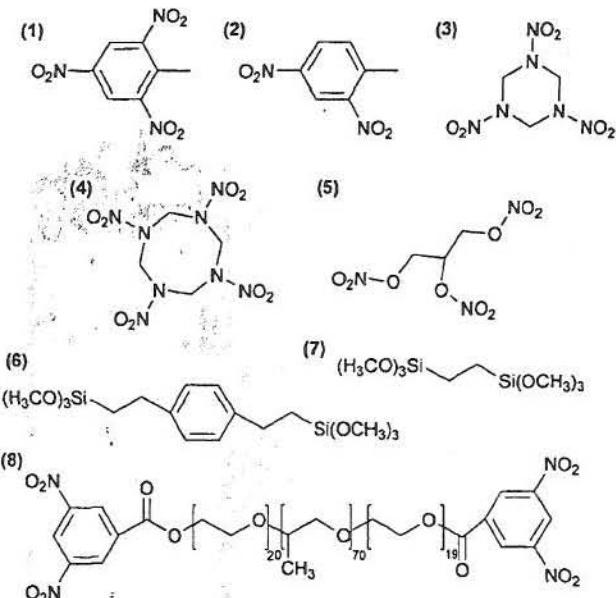


Fig. 1. Shown here are the molecular structures of the targets TNT (1), DNT (2), RDX (3), HMX (4), and NG (5). Also presented are the molecular structures of the precursors and structure directing molecules used in the synthesis of MM1: DEB (6), BTE (7), and the modified Pluronic P123 template (8).

surrounding munitions testing and training sites. Extraction of targets from solutions prepared using deionized water was evaluated in order to determine a baseline for sorbent performance. Target concentrations were selected to cover both those within the detection limits for the analytical method and those below the detection threshold (0.9 to 200 parts per billion (ppb)). For these samples a 20 mL target solution was applied to a 200 mg sorbent column. The column was rinsed using 6 mL deionized water and target was eluted in 4 mL acetonitrile. The column was rinsed with an additional 4 mL of acetonitrile and, finally, rinsed with 6 mL deionized water. Each of the 5 volumes was collected, and their target content was analyzed by HPLC.

Fig. 2 provides representative data on the target recovered in the first acetonitrile elution for each of the three sorbents, MM1, LiChrolut, and Sep-Pak, following exposure to 1 µg target in deionized water. Complete results of HPLC analysis are provided in the ESI (Table S1†). An optimal solid-phase extraction sorbent for application to in-line target preconcentration should capture compounds from dilute solution with little breakthrough and provide elution of those targets in a small volume of eluate. The result is a higher target concentration than that of the original sample, leading to enhanced detection limits. Overall, MM1 provided effective recovery of TNT (>85% from concentrations as low as 5 ppb), RDX (>92% from 5 ppb), DNT (>89% from 5 ppb) and NG (>87% from 50 ppb); results were comparable to recovery by LiChrolut. None of the three sorbents performed optimally for extraction of HMX, and the commercial materials showed poor recovery of NG. The Sep-Pak material demonstrated target breakthrough and bleeding of target into the second acetonitrile elution volume for nearly all compounds.

While the experiments in deionized water establish a baseline for sorbent performance, the samples do not reflect those

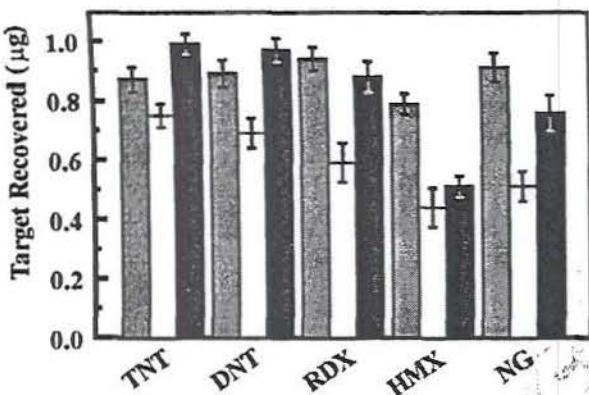


Fig. 2 Shown here is the target recovered in the first acetonitrile elution (4 mL) following application of target solutions in deionized water (20 mL) for each of the three sorbents, MM1 (gray), Sep-Pak (white), and LiChrolut (black). Total applied target is 1 µg.

encountered in a real-world sampling environment. In order to evaluate the impact of complex matrices on the performance of the sorbents, samples were prepared in artificial sea water, ground water, and surface water. Fig. 3 presents representative data on the target recovered by each sorbent from artificial sea water; data for other matrices are summarized in Table 1. Complete results are provided in the ESI (Table S2, S3, and S4†). The pH of the sea water samples was 6.0, identical to that of the deionized water samples. The recovery of TNT, DNT, and HMX from sea water was similar to recovery from deionized water for MM1 (Fig. 3); RDX recovery was slightly reduced. The lack of strong impact on sample recovery tends to indicate that binding of the targets by this sorbent is not sensitive to the ionic strength of the matrix. The recovery of RDX and HMX by LiChrolut was not impacted by the sea water while that of TNT and DNT was reduced in this matrix. Recovery of TNT, DNT, RDX, and HMX from sea water by Sep-Pak was not negatively impacted by the artificial sea water. In fact, recovery of targets was slightly greater than that from deionized water. The recovery of NG was

Table 1 Recovery of targets from various matrices^a

| | TNT | DNT | RDX | HMX | NG |
|----------------------|-----|-----|-----|-----|----|
| <i>Ground water</i> | | | | | |
| MM1 | 92 | 88 | 90 | 67 | 74 |
| Sep-Pak | 46 | 63 | 50 | 51 | 50 |
| LiChrolut | 60 | 73 | 71 | 41 | 59 |
| <i>Surface water</i> | | | | | |
| MM1 | 87 | 87 | 84 | 50 | 85 |
| Sep-Pak | 63 | 71 | 63 | 30 | 53 |
| LiChrolut | 83 | 89 | 90 | 51 | 54 |
| <i>pH 3</i> | | | | | |
| MM1 | 70 | 87 | 86 | 61 | 55 |
| Sep-Pak | 51 | 51 | 55 | 45 | 44 |
| LiChrolut | 56 | 59 | 63 | 42 | 47 |
| <i>pH 9</i> | | | | | |
| MM1 | 85 | 80 | 86 | 68 | 65 |
| Sep-Pak | 59 | 64 | 59 | 41 | 52 |
| LiChrolut | 62 | 80 | 84 | 59 | 62 |

^a Percentage of target recovered in the first acetonitrile elution (4 mL) following application of target solutions. Total applied target is 1 µg. Three-sigma variations for these analyses are between 7% and 10%.

negatively impacted for all three sorbents by the artificial sea water.

Surface water consists of ponds, lakes, streams, and other bodies of water that are over the surface of the land (typically excludes salt water bodies). Ground water is that in the zone of saturation of an aquifer or soil. Surface water often contains a number of contaminants such as industrial wastes and run-off from agricultural operations. Surface water also typically contains naturally occurring contaminants such as algae and bacteria resulting in a high concentration of dissolved organic carbon. Ground water may contain these contaminants, but often at lower levels owing to filtration by the soil. Ground water generally has a higher mineral content than surface water also as a result of soil contact. Surface water from a pond and ground water from a household well were used as representative matrices. In both cases, the water was filtered using Whatman GF/A glass fiber filters (1.6 µm particle retention) to remove large particulate prior to spiking with targets. Data on the recovery of targets from ground and surface water are presented in Table 1 (ESI, Table S3 and S4†). Recovery of TNT, DNT, and RDX from these samples by MM1 was similar to that from deionized water. Recovery of HMX was significantly less from both matrices while that of NG was reduced in only the ground water sample. For the LiChrolut material, recovery of TNT, DNT, and NG was negatively impacted by both matrices while that of HMX and RDX showed little change from the results in deionized water. Recovery of TNT and HMX by Sep-Pak was negatively impacted in both matrices.

Contaminant-free precipitation typically has a pH of 5.6; however, the pH of environmental water is often influenced by pollution (acid rain is one example) and the surrounding soil chemistry. In order to evaluate the effect of pH on the capture of targets by and recovery of targets from the SPE materials, samples in deionized water at pH 3.0 and pH 9.0 were evaluated (ESI, Table S5†). As shown in Table 1, the recovery of DNT and RDX using MM1 was not impacted by changes in the pH while HMX and NG recovery was significantly reduced at low pH.

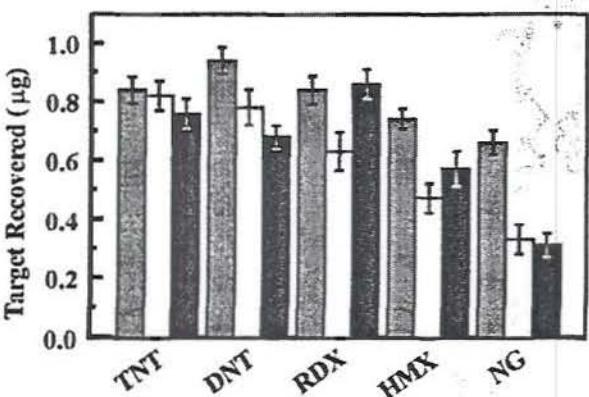


Fig. 3 Shown here is the target recovered in the first acetonitrile elution (4 mL) following application of target solutions in artificial sea water (20 mL) for each of the three sorbents, MM1 (gray), Sep-Pak (white), and LiChrolut (black). Total applied target is 1 µg.

Recovery of TNT by MM1 was reduced at pH 3 but not at pH 9. Recovery of targets by LiChrolut was significantly reduced at low pH; recovery of TNT, DNT and NG was reduced at pH 9. Altering the pH of the target solutions resulted in reduced binding of TNT by Sep-Pak but little change was observed for the other targets.

Soil samples with varying contaminants were obtained from sites of prior ordnance detonation. Sites varied in the size of ordnance and the age of the site. The samples were collected, air dried, ground, sub-sampled, and analyzed in accordance with EPA Method 8330B. Complete results of this analysis are provided in the ESI (Table S6†). A number of compounds were expected in these samples. In the case of the 2000 lb bomb crater, low-ordered scattering of tritonol was visible over hundreds of metres. Tritonal was exposed to the sun resulting in a reaction which produces trinitrobenzene (TNB) and 2,4-dinitroaniline (DNA) from the TNT. 2,4-Dinitrotoluene (DNT) is found as an impurity in TNT manufacturing and is employed as a propellant. Washing of TNT from the surface of the particles by precipitation results in a reaction which produces 2-amino-4,6-dinitrotoluene (2-ADNT) and 4-amino-2,6-dinitrotoluene (4-ADNT).

Subsamples of the dried soils were extracted overnight into water for evaluation of the target capture by MM1 from complex sample mixtures. Table 2 shows the results of MM1 capture and elution for sample HO-004 (25 mg sorbent column). This sample was taken from an aged 2000 lb bomb crater. The soil extract contained a high concentration of TNT and lower concentrations of RDX, 2-ADNT, 4-ADNT, and DNT (based on EPA Method 8330B analysis). When target was applied to the MM1 column, a small amount of TNT was found in the column effluent. This was expected as the total target applied exceeded the saturation capacity of the column. The concentration of TNT in the eluate was enhanced by nearly 10 times using the MM1 column. TNB, 2-ADNT, and 4-ADNT were not detected in the original extract but were found at detectable concentrations in the eluate. The concentration of RDX was enhanced by more than 7 times. This difference in the enhancement of TNT and RDX concentrations is related to the original concentrations of the targets as well as the relative affinity of the sorbent for the targets. Table 3 provides a qualitative summary of the results obtained for three soil samples including analysis by EPA Method 8330B and the results for application of the extracts to

the MM1 column. With the exception of TNT, which was often found at high concentrations, there was little bleeding of targets through the column and target recovery was consistent with that expected based on EPA Method 8330B analysis. In some instances (sample HO-020, for example), enhanced target concentrations made detection possible where the EPA method failed. Poor relative recovery and/or low water solubility of some targets (TNB, for example) lead to a failure to detect those compounds in the presence of competing targets. Complete results for all 12 soil samples are provided in the ESI (Table S7†). The targets in these complex mixtures were bound with varying affinity by the MM1 column leading to variations in the enhancement factor for the different compounds. In sample HO-001, for example, the concentration of TNT was enhanced by more than 8 times while that of RDX was enhanced by only a factor of 4. A similar effect was observed for the LiChrolut and Sep-Pak materials (ESI, Table S8†).

Experimental

Solutions of 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), nitroglycerin (NG), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) were prepared by dilution of 1 mg mL⁻¹ reference standards in acetonitrile obtained from Cerilliant (Round Rock, TX). Bis(trimethoxysilyl)benzene (DEB) and 1,2-bis(trimethoxysilyl)ethane (BTE) were obtained from Gelest, Inc. (Tullytown, PA). Sea salts, 3,5-dinitrobenzoyl chloride ≥98%, dichloromethane (≥99.5%), and magnesium turnings (98%) were purchased from Sigma-Aldrich (St Louis, MO). Pluronic P123 (referred to here as P123) was a gift from BASF (Mount Olive, NJ). Water was deionized to 18.2 MΩ cm using a Millipore Milli-Q UV-Plus water purification system. Artificial sea water was prepared using salts in deionized water (as directed by the supplier). Pond water was collected from a park in Alexandria, VA, USA. Ground water was collected from a well in Hanover, NH, USA. Soil samples collected from sites on Holloman Air Force Base, Alamogordo, NM and results of their analysis by EPA Method 8330B were provided by the Cold Regions Research and Engineering Laboratory, Engineer Research and Development Center, US Army Corps of Engineers.

Synthesis of the solid-phase extraction sorbent referred to as MM1 was accomplished using a variation on our previously reported technique^{41,44} and has been reported previously.⁴² Briefly, P123 (1.66 g) was combined with imprint template (0.24 g, 3,5-dinitrobenzoyl chloride modified P123; described previously^{41,42}) and mesitylene (TMB; 0.2 g) in 0.1 M HNO₃ (6 g) at 60 °C. The solution was allowed to cool prior to addition of a siloxane mixture consisting of 7.84 mmol total bis-silane (BTE + DEB at a 1 to 1 molar ratio). The mixture was stirred until homogeneous and transferred to a sealed culture tube. The tube was heated at 60 °C overnight (~18 h). The tube was unsealed and heated at 60 °C for a further 2 days followed by incubation at 80 °C for an additional 2 days. Product was refluxed in ethanol to extract the surfactant. The resulting powder was collected by suction filtration, rinsed, and dried. N₂ sorption experiments were performed using a Micromeritics ASAP 2010 at 77 K. Samples were degassed to 1 μm Hg at 100 °C prior to analysis. Surface area was determined by the Brunauer–Emmett–Teller

Table 2 Results of HPLC analysis for volumes resulting from pre-concentration of a soil sample (HO-004) by MM1 (25 mg column)^a

| Target concentration (ppm) ^b | | |
|---|-------------|-------------|
| As extracted | Effluent | Eluate |
| 2,4-DNT | — | — |
| 2-ADNT | — | 0.10 (0.01) |
| 4-ADNT | — | 0.24 (0.03) |
| DNB | — | — |
| HMX | — | — |
| RDX | 0.01 (0.01) | 0.07 (0.01) |
| TNB | — | 0.01 (0.01) |
| TNT | 0.25 (0.03) | 2.87 (0.18) |

^a Volume applied 20 mL; eluate volume 2 mL. ^b Value in parenthesis is equal to 3 × the standard deviation for the measurement.

Table 3 Qualitative summary of results for selected soil samples comparing targets detected using the standard EPA Method 8330 with results of HPLC analysis of the aqueous soil extract, the preconcentration column effluent and the concentrated eluent^a

| | | Target detected | | HMX | RDX | TNB | DNB | TNT | 2-ADNT | 4-ADNT | 2,4-DNT |
|--------|--------------|-----------------|--|-----|-----|-----|-----|-----|--------|--------|---------|
| HO-001 | Method 8330B | | | | | X | | X | X | X | X |
| | Extract | | | X | | X | | X | | | X |
| | Effluent | | | X | | X | | X | | | X |
| | Eluate | | | X | | X | | X | X | X | X |
| HO-020 | Method 8330B | | | | | | | X | X | X | |
| | Extract | | | | | | | X | | | |
| | Effluent | | | | | | | X | | | |
| | Eluate | | | | | | | X | | | |
| HO-026 | Method 8330B | X | | | | X | | X | X | X | X |
| | Extract | | | | | X | | X | | | |
| | Effluent | | | | | | | X | | | |
| | Eluate | | | | | | | X | X | | |

^a 'X' indicates target detected.

(BET) method, pore size calculated by the Barrett-Joyner-Halenda (BJH) method from the adsorption branch of the isotherm, and total pore volume by single-point method at relative pressure (P/P_0) 0.97. Results of characterization for this material as well as the LiChrolut and Sep-Pak sorbents are provided in the ESI (Fig. S1†). The BET surface area for MM1 was found to be $439 \text{ m}^2 \text{ g}^{-1}$ with a BJH pore volume of $0.399 \text{ cm}^3 \text{ g}^{-1}$ and an average mesopore diameter of 36 \AA .

Columns of the sorbent materials were prepared in BioRad disposable polypropylene columns using 25 or 200 mg of sorbent as specified. Controlled flow (4 mL min^{-1}) experiments were conducted. HPLC analysis of the various elution volumes was used to determine target concentrations. Elution of targets from the columns was accomplished using acetonitrile or methanol as indicated. LiChrolut EN (LiChrolut; VWR International) and Sep-Pak RDX (Sep-Pak; 125–150 μm ; Waters Corporation, Milford, MA) materials were handled identically to the sorbents prepared in-house. This protocol adhered to the manufacturer recommendations for the commercial sorbents. Soil sample extracts were prepared by overnight incubation of 2 g soil in 20 mL deionized water on a rotisserie mixer. Prior to analysis, the heavy particulate was allowed to settle out of solution, and the solution was filtered using a $0.2 \mu\text{m}$ PTFE syringe filter to remove any remaining insoluble material.

Analysis of samples was carried out on a Shimadzu High Performance Liquid Chromatography (HPLC) system with dual-plunger parallel flow solvent delivery modules (LC-20AD) and an auto-sampler (SIL-20AC) coupled to a photodiode array detector (SPD-M20A). A modification of EPA method 8330 was employed. The stationary phase was a $250 \times 4.6 \text{ mm}$ Altech Alltima C18 (5 μm) analytical column; an isocratic 50 : 50 methanol : water mobile phase was employed. A $100 \mu\text{L}$ sample injection was used with a flow rate of 1.3 mL min^{-1} . UV/vis detection of targets was accomplished at 254 nm with the exception of nitroglycerin which was detected at 214 nm. This method gives reliable detection at 8 ppb for the targets considered. Eight point target calibration curves were used with all experiments to verify method performance, and stock target concentrations were measured as a reference for each experiment. The variation in the calibration curves was $\pm 5\%$.

Conclusions

Over all, MM1 showed better performance than the Sep-Pak material recovering a greater percentage of the target applied and yielding a more concentrated eluate. Unlike the Sep-Pak material, there was very little target breakthrough into the effluent or leakage into the rinse volumes. LiChrolut showed slightly better performance for recovery of targets from deionized water than MM1, however, recovery by LiChrolut was strongly impacted by alterations to the sample matrix. MM1 was shown to offer consistent recovery of TNT, DNT, and RDX across a range of matrices with greater variation in the recovery of HMX and NG. The results here demonstrate that the novel sorbent offers enhanced performance over the commercially available materials. The intended application for the new sorbent is in the preconcentration of targets for *in situ* monitoring of contaminants in water sources. When the relevant matrices are considered, MM1 provides 24% and 14% greater target recovery on average than Sep-Pak and LiChrolut, respectively. In addition, further enhancements to the performance of MM1 type sorbents may be possible through additional tuning of the structural characteristics or through variation in the imprinting process. MM1 was imprinted with an analog of 3,5-dinitrotoluene. The idea was to influence the surface so that interaction with nitro groups on an aromatic ring would be favored. This approach is not necessarily optimal for increasing the selectivity or capacity of the material for binding of RDX, HMX, or NG. While MM1 has some structural features on the macroscale,⁴² it is possible to develop that structure further.⁴³ A larger, more open structure may help to facilitate diffusion of targets throughout the sorbent allowing for more effective utilization of the surface area of the material. In addition, the relatively low surface area of MM1 ($439 \text{ m}^2 \text{ g}^{-1}$ as compared to $683 \text{ m}^2 \text{ g}^{-1}$ for similar materials⁴³) indicates the potential for increased order on the mesoscale which, in addition to offering additional sites for interaction, should also provide enhanced access to the available surfaces.

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